United States
Environmental Protection
Agency

Office of Research and
Development
Washington DC 20460

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EPA

Innovative Technology Verification Report

Field Measurement Technology for Mercury in Soil and Sediment

Ohio Lumex's RA-915/RP-91C Mercury Analyzer - May 2004

DMA-80 Non portable. Good precision, accuracy
PDV 6000 Requires sample digestion, generates waste stream! Acceptable accuracy, good precision

SITE

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MEASUREMENT AND MONITORING TECHNOLOGY PROGRAM VERIFICATION STATEMENT

TECHNOLOGY TYPE: **Field Measurement Device**

APPLICATION: **Measurement for Mercury**

TECHNOLOGY NAME: **Ohio Lumex Co.'s RA-915+/RP-91C Mercury Analyzer**

COMPANY: **Ohio Lumex Co.**
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VERIFICATION PROGRAM DESCRIPTION

The U.S. Environmental Protection Agency (EPA) created the Superfund Innovative Technology Evaluation (SITE) and Measurement and Monitoring Technology (MMT) Programs to facilitate deployment of innovative technologies through performance verification and information dissemination. The goal of these programs is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. These programs assist and inform those involved in design, distribution, permitting, and purchase of environmental technologies. This document summarizes results of a dem onstration of the RA-915+/RP-91C Mercury Analyzer developed by Ohio Lumex Co.

PROGRAM OPERATION

Under the SITE and MMT Programs, with the full participation of the technology developers, the EPA evaluates and documents the performance of innovative technologies by developing demonstration plans, conducting field tests, collecting and analyzing demonstration data, and preparing reports. The technologies are evaluated under rigorous quality assurance (QA) protocols to produce well-documented data of known quality. The EPA National Exposure Research Laboratory, which demonstrates field sampling, m onitoring, and m easurement technologies, selected Science Applications International Corporation as the verification organization to assist in field testing five field measurement devices for mercury in soil and sediment. This demonstration was funded by the SITE Program.

DEMONSTRATION DESCRIPTION

In May 2003, the EPA conducted a field demonstration of the RA-915+/RP-91C and four other field measurement devices for mercury in soil and sediment. This verification statement focuses on the RA-915+/RP-91C; a similar statement has been prepared for each of the other four devices. The performance of the RA-915+/RP-91C was compared to that of an off-site laboratory using the reference method, "Test Methods for Evaluating Solid Waste" (SW-846) Method 7471B (modified). To verify a wide range of perform ance attributes, the demonstration had both primary and secondary objectives. The primary objectives were:

(1) Determining the instrument sensitivity with respect to the Method Detection Limit (MDL) and Practical Quantitation Limit (PQL);
(2) Determining the analytical accuracy associated with the field measurement technologies;
(3) Evaluating the precision of the field measurement technologies;
(4) Measuring the amount of time required for mobilization and setup, initial calibration, daily calibration, sample analysis, and demobilization; and
(5) Estimating the costs associated with mercury measurements for the following four categories: capital, labor, supplies, and investigation-derived waste (IDW).

Secondary objectives for the demonstration included:

(1) Documenting the ease of use, as well as skills and training required to properly operate the device;
(2) Documenting potential health and safety concerns associated with operating the device;
(3) Documenting the portability of the device;
(4) Evaluating the device durability based on its materials of construction and engineering design; and

(5) Documenting the availability of the device and associated spare parts.

The RA-915+/RP-91C analyzed 56 field soil samples, 26 field sediment samples, 42 spiked field samples, and 73 performance evaluation (PE) standard reference material (SRM) sam ples in the demonstration. The field sam ples were collected in four areas contam inated with mercury, the spiked samples were from these same locations, and the PE samples were obtained from a commercial provider.

Collectively, the environmental and PE samples provided the different m atrix types and the different concentrations of mercury needed to perform a comprehensive evaluation of the RA-915+/RP-91C. A complete description of the demonstration and a summary of the results are available in the Innovative Technology Verification Report: "Field Measurement Technology for Mercury in Soil and Sediment—Ohio Lum ex Co.'s RA-915+/RP-91C Mercury Analyzer" (EPA/600/R-03/147).

TECHNOLOGY DESCRIPTION

The RA-915+ Mercury Analyzer is a portable AA spectrometer with a 10-meter (m) multipath optical cell and Zeeman background correction. Mercury is detected without preliminary accumulation on a gold trap. Mercury samples are heated to 750-800°C, causing organic materials to be decomposed and mercury to be vaporized in a carrier gas of ambient air. The airflow carries the vaporized mercury to be carried to the analytical cell . The RA-915+ includes a builtin test cell for field performance verification. The operation of the RA-915+ is based on the principle of differential, Zeeman AA spectrometry combined with high-frequency modulation of polarized light. This combination eliminates interferences and provides the highest sensitivity. A mercury lamp is placed in a permanent magnetic field in which the 254-nm resonance line is split into three polarized components, two of which are circularly polarized in the opposite direction. These two components (F- and F+) pass through a polarization modulator, while the third component (B) is removed. One F component passes through the absorption cell; the other F component passes outside of the absorption cell and through the test cell. In the absence of mercury vapors, the intensity of the two F components are equal. When mercury vapor is present in the absorption cell, mercury atoms cause a proportional, concentration-related difference in the intensity of the F components. This difference in intensity is what is measured by the instrument. The unit can be used with the optional RP-91C for an ultra-low mercury detection limit in water samples using the "cold vapor" technique. For direct mercury determination in complex matrices without sample pretreatment, including liquids, soils and sediments, the instrument will be operated with the optional RP-91C accessory, as was done during the demonstration.

During the demonstration, no extraction or sample digestion was required. Individual samples were mixed manually using a quartz injection spoon. This same spoon was used to transfer the sample directly to the RP-91C sample injection port after the sample was weighed on a digital balance. The sample weight was manually recorded. The sample was analyzed, and the device displayed the mercury concentration in parts per million, which is equivalent to a soil concentration in milligrams per kilogram.

ACTION LIMITS

Action limits and concentrations of interest vary and are project specific. There are, however, action limits which can be considered as potential reference points. The EPA Region IX Preliminary Remedial Goals for mercury are 23 mg/kg in residential soil and 310 m g/k g in industrial soil.

VERIFICATION OF PERFORMANCE

To ensure data usability, data quality indicators for accuracy, precision, representativeness, completeness, comparability, and sensitivity were assessed for the reference method based on project-specific QA objectives. Key demonstration findings are summarized below for the primary objectives.

***Sensitivity*:** The two primary sensitivity evaluations performed for this demonstration were the MDL and PQL. Both will vary dependent upon whether the matrix is a soil, waste, or aqueous solution. Only soils/sediments were tested during this demonstration, and therefore, MDL calculations and PQL determinations for this evaluation are limited to those matrices. By definition, values measured below the PQL should not be considered accurate or precise and those below the MDL are not distinguishable from background noise.

Method Detection Limit - The evaluation of an MDL requires seven different measurements of a low concentration standard or sample following the procedures established in the 40 Code of Federal Regulations (CFR) Part 136. The MDL is estimated between 0.0053 and 0.042 mg/kg. The equivalent MDL for the referee laboratory is 0.0026 mg/kg.

Practical Quantitation Limit - The low standard calculations using MDL values suggest that a PQL for the Ohio Lumex field instrument may be as low as 0.027mg/k g (5 times the lowest calculated MDL). The %D for the average Ohio Lumex result for a tested sample with a referee laboratory value of 0.06 mg/k g is 0.072 mg/k g, with a %D of 20%. This was the lowest sample concentration tested during the demonstration that is close to but not below, the calculated PQL noted above. The referee laboratory PQL confirmed during the demonstration is 0.005 mg/kg with a %D <10%.

***Accuracy*:** The results from the RA-915+/RP-91C were compared to the 95% prediction interval for the SRM materials and to the referee laboratory results (Method 7471B). The Ohio Lumex data were within SRM 95% prediction intervals 93% of the time, which suggests significant equivalence to certified standards. The comparison between the Ohio Lumex field data and the referee laboratory results suggest that the two data sets are not the same. When a unified hypothesis test is performed (which accounts for laboratory bias), this result is confirmed. Ohio Lumex data were found to be both above and below referee laboratory concentrations, therefore there is no implied or suggested bias. The number of Ohio Lumex average values less than 30% different from the referee laboratory results or SRM reference values was significant – 19 of 33 different sample lots. Ohio Lumex results therefore, provide accurate estimates for field determination. Because the Ohio Lumex data compare favorably to the SRM values, the differences between Ohio Lumex and the referee laboratory are likely the result of reasons beyond the scope of this study.

***Precision*:** The precision of the Ohio Lumex field instrument is better than the referee laboratory precision. The overall average RSD, is 22.3% for the referee laboratory compared to the Ohio Lumex average RSD of 16.1%. This is primarily because of the better precision obtained for the SRM analyses by Ohio Lumex. Both the laboratory precision and the Ohio Lumex precision goals of 25% overall RSD were achieved.

***Measurement Time*:** From the time of sample receipt, Ohio Lumex required approximately 21 hours, 15 minutes, to prepare a draft data package containing mercury results for 197 samples. One technician performed half of the equipment setup and demobilization, most of the sample preparation, and all of the analyses. Individual analyses took 1 minute each, but the total time per analysis averaged 8.1 minutes per sample (based upon 1.25 analysts) when all field activities and data package preparation were included in the calculation because the vendor chose to analyze replicates of virtually every analysis.

***Measurement Costs*:** The cost per analyses based upon 197 samples, when renting the RA-915+/RP-91C, is $23.44 per sample. The cost per analyses for the 197 samples, excluding rental fee, is $15.82 per sample. Based on a 3-day field demonstration, the total cost for equipment rental and necessary supplies is estimated at $4,617. The cost by category is: capital costs, 32.5%; supplies, 10.8%; support equipment, 6.0%; labor, 19.5%; and IDW, 31.2%.

Key demonstration findings are summarized below for the secondary objectives.

***Ease of Use*:** Based on observations made during the demonstration, the RA-915+/RP-91C is reasonably easy to operate; however, lack of automation somewhat impairs the ease of use. Operation requires one field technician with a basic knowledge of chemistry acquired on the job or in a university and training on the instrument.

***Potential Health and Safety Concerns*:** No significant health and safety concerns were noted during the demonstration. The only potential health and safety concerns identified were the generation of mercury vapors and the potential for burns with careless handling of hot quartz sample boats. The vendor provides a mercury filter as standard equipment; exercising caution and good laboratory practices can mitigate the potential for burns.

***Portability*:** The RA-915+ air analyzer was easily portable, although the device, even when carried in the canvas sling, was not considered light-weight. The addition of the RP-91C and associated pump unit preclude this from being a truly field portable instrument. The device and attachments can be transported in carrying cases by two people, but must then be set up in a stationary location. It was easy to set up, but the combined instrument is better characterized as mobile rather than field portable.

Durability: The RA-915+/RP-91C was well designed and constructed for durability. The outside of the RA-915+ is constructed of sturdy aluminum and the exterior of the RP-91C furnace is stainless steel.

Availability of the Device: The RA-915+/RP-91C is readily available for rental, lease, or purchase. Spare parts and consumable supplies can be added to the original instrument order, or can be received within 24 to 48 hours of order placement. Standards are readily available from laboratory supply firms or can be acquired through Ohio Lumex.

PERFORMANCE SUMMARY

In summary, during the demonstration, the RA-915+/RP-91C exhibited the following desirable characteristics of a field mercury measurement device: (1) good accuracy compared to SRMs, (2) good precision, (3) good sensitivity, (4) high sample throughput, (5) low measurement costs, and (6) ease of use. During the demonstration the RA-915+/RP-91C was found to have the following limitations: (1) lack of automation and (2) non-portable due to the instrument size and weight. The demonstration findings collectively indicated that the RA-915+/RP-91C is a reliable field measurement device for mercury in soil and sediment.